California Environmental Protection Agency

Air Resources Board

SOP MLD 016

STANDARD OPERATING PROCEDURE FOR THE MASS ANALYSIS AND SUBSEQUENT EXTRACTION OF SSI-SAMPLED PM_{10} FROM EXPOSED QUARTZ MICROFIBRE FILTERS

Northern Laboratory Branch
Monitoring and Laboratory Division

First Approved Date of SOP: May 1, 1986
Approval Date of Last SOP Amendment: November 13, 2007
Revision Number: 6.0

Table of Contents

SOP MLD 016

STANDARD OPERATING PROCEDURE (SOP) FOR THE MASS ANALYSIS AND SUBSEQUENT EXTRACTION OF SSI-SAMPLED PM_{10} FROM EXPOSED QUARTZ MICROFIBRE FILTERS

1.0 SCOPE

This document details the mass analysis and water extraction of particulate matter less than or equal to ten micrometers in mean aerodynamic diameter (PM_{10}) from exposed quartz microfibre filters. It combines and supersedes SOP NSL016, Revision No. 5.0 (January 18, 2002) and SOP MLD 030 (April 1, 1990).

2.0 SUMMARY OF METHOD

Before field sampling, individual quartz microfibre filters are weighed on an electronic balance that is interfaced to the Laboratory Information Management System (LIMS). PM_{10} is collected from ambient air over a 24-hour period on the quartz microfibre filters. The filters are then post-weighed, and the concentration of PM_{10} particles in the air in $\mu g/m^3$ is calculated based on the total volume of air drawn through the filter. For samples that undergo ion analysis, one quarter of the exposed area is cut from the filter. Water-soluble compounds deposited on this filter section are extracted by vigorous shaking in purified water. The extraction solution is vacuum filtered, bottled and stored for later analysis by ion chromatography (Refer to SOP MLD068, Revision No. 0, which combines and supersedes methods MLD007 and MLD023).

Total Suspended Particulate (TSP) samples are collected from ambient air over a 24-hour period on glass microfibre filters. The filters are extracted with dilute nitric acid and the solution is determined for lead concentrations using atomic absorption (AA) spectrophotometry (Refer to SOP MLD005, Revision 6.1 for more information). Although gravimetric analysis and sulfate extractions are no longer performed for TSP samples, the same procedures used for PM_{10} samples can be applied. Likewise, the criteria given in this SOP for filter inspections (See Appendix A) and for quality control (See Appendix B) are also applicable to the TSP program.

3.0 INTERFERENCES

3.1 Fingerprints may increase the mass of and contaminate the quartz filters, therefore powder-free antistatic gloves must be worn when handling quartz filters.

3.2 Static electricity will build up on the quartz filters causing erroneous mass results and/or a failure of the balance reading to stabilize. Because of this, two Staticmaster® anti-static devices are kept in the balance weighing chamber in order to dissipate static charge. These devices must be replaced annually in order to maintain effectiveness. Additionally, only antistatic gloves are used while handling the filters.

3.3 The moisture content of a filter affects its weight. Because of this, filters are equilibrated in a conditioning environment (32 - 42% RH, 18.3 - 24.3°C) for at least 24 hours before being weighed. If the percent relative humidity or temperature falls outside of this range, the 24-hour equilibration period is started over once the environmental conditions are back in control.

The temperature and relative humidity are recorded on a Honeywell humidity/temperature weekly chart recorder. The humidity/temperature recorder is calibrated every three months using a National Institute of Standards and Technology (NIST)-traceable humidity/temperature monitor. The % RH and temperature in °C must be within ±2 of the NIST standard value.

3.4 Contamination of samples can occur from failure to clean the cutting board and scissors. All cutting equipment should be wiped thoroughly with a new dry laboratory wipe prior to each use.

3.5 Regular tap water or deionized tap water may cause contamination. For sample preparation and extraction rinsing use only water that is deionized and monitored for resistivity using a water purification system. The purified water must have a resistivity of greater than 10 MΩ. For simplicity purposes, water meeting these qualifications will be referred to as nanopure.

3.6 For ion analysis, unexposed filter pieces are used as background media for method blanks and spikes. Individual, unexposed filters should be quartered and the pieces placed together in a glassine enclosure. Place each enclosure in its own numbered (e.g., 1-10) manila folder. If there is a contaminated blank filter this will enable us to identify which filter is contaminated. These filter pieces must be stored such that they remain free of contaminants such as dust.

3.7 All glassware and sample bottles, including lids, should be washed thoroughly using a non-foaming liquid detergent and rinsed with nanopure water prior to use. Using excess dishwasher detergent may affect ion concentrations.

4.0 APPARATUS AND MATERIALS

4.1 High purity quartz microfibre filters (Whatman® QMA, 8''x10'')

4.2 High purity glass microfibre filters (Whatman® EPM, 8''x10'')

4.3 Light box, 16" x 18"

4.4 Analytical Balance with a minimum resolution of 0.1 mg and minimum precision of 0.5 mg equipped with an RS232 interface and glass enclosure (Sartorius A200S) that is certified annually

4.5 Filter weighing rack for use with the balance

4.6 Two sets of Ainsworth 1 g, 3 g, and 5 g Class S weights with plastic forceps. One set (the reference set) should be NIST certified annually. The other set (the working set) should be checked against the reference set quarterly.

4.7 Staticmaster® antistatic devices

4.8 Computer terminal interfaced to SQL*LIMS with IDM LimsLink™ v3.1 and Microsoft® Excel

4.9 Humidity and Temperature Recorder/Controller (Honeywell DR4500A)

4.10 NIST-traceable instrument for determining humidity and temperature, calibrated annually

4.11 Water Purification System (Barnstead NANOpure® Diamond™ UV system with Diamond Cartridge Pack D50281)

4.12 Water delivery system with a minimum precision in the 100 mL range of 0.3 mL (Wheaton Unispense® II)

4.13 Dispensing jug, polypropylene or high-density polyethylene, 20 L capacity

4.14 Erlenmeyer flasks, 250 mL, with ground-glass stoppers

4.15 Sample bottles, 125mL, polypropylene or high-density polyethylene, with screw-top lids

4.16 Cutting board with ruled edges

4.17 Scissors, long edge

4.18 Filter base with CTFE fittings (Kontes 953872-0000) and a 2000 mL filter dome (Kontes 953871-2000) tooled to accept a 300 mL capacity polysulfone magnetic filter funnel (Pall Life Sciences 4241)

4.19 Sterile filtration membranes, 47 mm diameter, 0.45 μm pore diameter (Pall Life Sciences, Metricel® Grid)

4.20 Shaker table with prongs fitted for 250 mL Erlenmeyer flasks

4.21 Dishwasher with deionized water rinse capability and steam cycle

4.22 Non-foaming, phosphate-free detergent (Alconox 8)

4.23 Refrigerator with multiple shelves

4.24 Micropipettor with 2.5 mL capacity tips

4.25 Miscellaneous: Manila folders (9" x 12", 5th cut); glassine enclosures (8 1/2"x 10 1/2", side cut); Sample Report forms; disposable laboratory wipes; self-adhesive labels; clock or timer; powder-free antistatic gloves; Teflon®-tipped forceps; pipette tips; bleach

5.0 FILTER INSPECTION AND PRE-WEIGHING PREPARATION PROCEDURE

5.1 High purity quartz microfibre filters (Whatman® QMA, 8''x10'') for PM_{10} sampling and high purity glass microfibre filters (Whatman® EPM, 8''x10'') for TSP sampling are received from the U.S. EPA. All filters are inspected for manufacturing defects by viewing both sides of the filter using a light table. See Appendix A for detailed filter inspection procedures and criteria.

5.2 Place a filter into a manila folder, followed by a glassine enclosure (8 1/2" x 10 1/2", side cut) and a Sample Report form. Repeat this process 16 times in order to make a packet.

5.3 For quartz filters, place the filters in the Balance Room with the folders oriented with the open edge up so that equilibration can occur more readily. Allow the filters to equilibrate at least 24 hrs prior to

pre-weighing (See Section 3.3 for Balance Room environmental requirements). Glass filters are not weighed, making equilibration in the balance room unnecessary.

6.0 BALANCE CALIBRATION PROCEDURE

6.1 Before calibrating the balance, check that the temperature and relative humidity of the Balance Room have remained within the allowable limits (See Section 3.3) for the last 24 hrs. Calibrate the balance each day prior to filter weighing. Perform all calibrations and weighings with the glass enclosure door closed.

6.2 Clean the balance pan and the filter holder with a soft brush. Check the bubble level on the balance to make sure that it is level; re-level if necessary. Remove the filter holder and tare the balance by pushing the 'T' button. Wait for the display to read 0.0000 g. Then push the 'CAL' button and wait for the display to read 0.0000 g.

6.3 Open IDM LimsLink™ v3.1 (hereafter referred to as LimsLink™) and login using your username and password. Click on the running man icon and select the 'Calibration' method. Select the worksheet for the current quarter and press 'OK'. If necessary, press 'Start New' and name the worksheet after the current quarter, e.g., 1st Q 2006. Press the green triangle in order to establish a connection between the balance and the program. If the green triangle is grayed out and the red square is present, then the connection has already been established.

6.4 Place the filter holder back onto the balance pan, push the 'T' button, and wait for the display to read 0.0000 g. Then place the 1 g and 3 g Class S weights onto the filter holder, close the balance enclosure door, and wait until the display stabilizes. Press the 'PRINT' button on the balance to send the weight information to the LimsLink™ worksheet. The weight must be 4.0000 ± 0.0005 g. Type the current temperature in °C and % RH into the worksheet. The temperature and % RH must be within the control limits (See Section 3.3).

6.5 If the weight falls outside of the range, repeat Sections 6.2 and 6.4. If the weight still falls outside of the range, then discontinue weighing and contact the lab manager immediately.

6.6 In LimsLink™ the sample status should read 'OK to Transfer'. Click on the 'Options' menu, 'Report1', then 'Send weight(s) to LIMS'. The field to the right of the sample status should read 'Sent to LIMS'. After a few minutes, click on the 'Options' menu, then

'LabODB3C', 'Retrieve Sample Status'. The sample status should say 'Complete'.

7.0 FILTER PRE-WEIGHING PROCEDURE

7.1 Before pre-weighing filters, check that the temperature and relative humidity of the Balance Room have remained within the allowable limits (See Section 3.3) for the last 24 hrs. Be sure that the balance has been calibrated (See Section 6.0) on the day you are weighing. The balance display should read 0.0000 g prior to each weighing (re-tare if necessary). Any filter weighing less than 3.7 g or more than 4.7 g should be investigated immediately, and will not used for sampling (U.S. Environmental Protection Agency. 1997. Quality Assurance Guidance Document 2.11, Monitoring PM_{10} in Ambient Air Using a High-Volume sampler Method).

7.2 Open LimsLink™ and login using your username and password. Click on the running man icon and choose the 'PM10 Pre-Weight with Controls' method. Click 'Start New' in order to create a new worksheet. A window will pop up with a 'Description' field; this is where the name of the new worksheet is entered. The worksheet name should be the date followed by the analyst's login name, e.g., 7/19/05 epresley. Click 'OK'.

7.3 Every filter has a factory-stamped serial number (filter number) that begins with a 'Q'. Enter the filter numbers, with the 'Q' omitted, in numerical order in the 'filter #' field. Press the green triangle in order to establish a connection between the balance and the program. If the green triangle is grayed out and the red square is present, then the connection has already been established.

7.4 Click on the 'Options' menu, 'Custom Program', then 'Insert Dups/Controls'. This will add the necessary duplicate and control weighings to your sample worksheet.

7.5 The first sample on your worksheet should be listed as 'ctl3'. Remove a 3 g Class S calibration weight with the provided plastic forceps and place it on top of the filter holder near the middle. When the weight has stabilized, transfer it to LimsLink™ by pressing the 'PRINT' button on the balance. Remove the weight and return it to its container.

7.6 The next sample on the worksheet should be listed as 'ctl5'. Repeat the procedure as stated for 'ctl3', except use a 5 g Class S calibration weight. Perform the other control weighings in this way as they occur

throughout the sample worksheet. Control weighings must be within ±0.0005 g of the known value. If the control difference limit is exceeded, the previous eight filters and duplicate must be re-weighed.

7.7 Using powder-free antistatic gloves, remove the first filter from its folder and carefully place it into the filter holder on the balance pan. Be cautious as edges of the filter are easily damaged. Do not allow the filter to rest against the glass enclosure as this will affect the weight. Close the glass door and wait for the balance to stabilize. The weight should be stabilized for a minimum of five seconds before transferring the weight to LimsLink^{TM} by pressing the 'PRINT' button on the balance.

7.8 Copy the displayed filter number and pre-weight onto the Sample Report form. Initial and date the Sample Report form in the bottom right corner under 'PRE-ANA'.

7.9 Remove the filter from the balance and place it in its folder, behind the protective glassine. Place the Sample Report form on top of the glassine. Close the glass enclosure and make sure that the balance display reads 0.0000 g. Repeat Sections 7.7 and 7.8 for the remaining filters.

7.10 Every eighth filter is re-weighed as a quality control check (duplicate). Duplicates (denoted by Rep # 2 in LimsLink^{TM}) are weighed in precisely the same manner. Write the duplicate weight to the right of the first pre-weight on the Sample Report form. The duplicate difference limit for PM_{10} pre-weights is $\pm$ 0.0028 g. If the duplicate difference limit is exceeded, the previous eight filters and duplicate must be re-weighed.

7.11 When pre-weighing is complete, click on the 'Options' menu, 'Reports1', then 'Add Controls to LIMS'. After a few minutes click on the 'Options' menu, 'LabODB3C', then 'Retrieve Sample Status'. The status of the control weights in LimsLink^{TM} should be listed as 'OK to LIMS'. Click on the 'Options' menu, 'Report1', then 'Send Ctl Results to LIMS'. After a few minutes click on the 'Options' menu, 'LabODB3C', then 'Retrieve Sample Status'. The status of the control weights in LimsLink^{TM} should be listed as 'Complete'. The status of the pre-weights in LimsLink^{TM} should be listed as 'OK to Transfer'. Click on the 'Options' menu, 'LabODB3C', then 'Send Pre-Wts to LIMS'. The field to the right of the pre-weight should read 'Sent to LIMS'. After a few minutes click on the 'Options' menu, 'LabODB3C', then 'Retrieve Sample Status'. The sample status for

all pre-weights should be 'Complete'.

7.12 To verify that all data was transferred and all quality control (QC) parameters were met, run the 'PM10 PreWeight Summary Report'. Double-click on the desktop shortcut 'Reports' and login. Click on 'File', 'Run', and double-click on 'PM10-PreWeight Summary.rep'. Enter the correct pre-weight date and click on the green stoplight icon to run the report. Check the report to verify that duplicates are acceptable (± 0.0028 g), the duplicate percentage is acceptable (≥10% according to Monitoring and Laboratory Division's (MLD) Northern Laboratory Branch (NLB) Laboratory Quality Control Manual (June 2001, rev. 2.4)), and control weighings are acceptable (±0.0005 g of the known value). Note that although the duplicate percentage must be ≥10%, since we perform a duplicate for every eight filters the duplicate percentage should be exactly 12.5%.

8.0 FILTER LOGIN PROCEDURE

8.1 All filters received from the field must be inspected prior to being logged into LIMS. While wearing powder-free antistatic gloves, remove a filter from its protective glassine enclosure and unfold it (filters are folded in half by the field staff). Inspect the filter, Dickson chart, and Sample Report for any issues that may cause invalidation of the sample using the criteria laid out in Appendix B. If the filter is invalid record the reason for invalidation in the comments section of the Sample Report form. Also put a red asterisk on the tab of the manila folder to indicate that the sample is invalid.

8.2 Return the filter, folded in half, to its manila folder with the filter number facing up. Place the Dickson chart on top of the glassine enclosure with midnight at the very top, put the Sample Report form on top of the Dickson chart, and staple them all together and place them on top of the filter.

8.3 Fill out the 'Sample Tracking' portion of the Sample Report form as indicated. Check the date and site name written on the outside of the folder and make sure that they match the information given on the Sample Report form. When the inspection is complete, initial and date the form in the bottom right corner under 'POST-ANA'.

8.4 Organize the manila folders alphabetically and affix barcode labels to them. The barcodes for all PM_{10} samples should be sequential and contiguous. The barcodes for all TSP samples should be sequential and contiguous as well.

8.5 Login to LIMS. Select 'Log', 'Enter', then 'By Sample'. Double-click the field next to 'Sample Plan' and choose the appropriate site and program. Double-click the cell next to 'User Sample ID', move the cursor to the field next to 'Barcode', and scan in the barcode. Enter the remainder of the information required by LIMS, which is obtained from the Sample Report form. Record the LIMS Sample ID on the Sample Report form in the indicated area.

8.6 For PM_{10} samples, place the folders in an area where they can equilibrate in preparation for post-weighing. Orient the folders with the open edge up so the equilibration can occur more readily.

9.0 FILTER POST-WEIGHING PROCEDURE

9.1 Before post-weighing filters, check that the temperature and relative humidity of the Balance Room have remained within the allowable limits (See Section 3.3) for the last 24 hrs. Be sure that the balance has been calibrated (See Section 6.0) on the day you are weighing. The balance display should read 0.0000 g prior to each weighing (re-tare if necessary).

9.2 Login to LimsLink™. Click on the running man icon and choose the 'PM10 Post-Weight' method. Click 'Start New' in order to create a new worksheet. A window will pop up with a 'Description' field, enter the name of the new worksheet. The worksheet name should be the date followed by the analyst's login name, e.g., 7/19/05 epresley. Click 'OK'.

9.3 Click on the 'Options' menu, 'LabODB3C', then 'Retrieve PM_{10} Samples'. A list is generated of all PM_{10} samples to be weighed. Click on the 'Options' menu, 'Custom Program', then 'Insert Dups/Controls'. This will add the necessary duplicate and control weighings to your sample worksheet. A duplicate sample is added for every nine filters to be weighed. If the number of filters to be weighed is not divisible by nine then there will be a set of less than nine filters with a replicate on the end of the list. Press the green triangle in order to establish a connection between the balance and the program. If the green triangle is grayed out and the red square is present, then the connection has already been established.

9.4 The first sample on your worksheet should be listed as 'ctl3'. Remove a 3 g Class S calibration weight with the provided plastic forceps and place it on the filter holder near the middle. When the weight has stabilized, transfer it to LimsLink™ by pressing the 'PRINT' button on the balance. Return the weight to its container.

9.5 The next sample on the worksheet should be listed as 'ctl5'. Repeat the procedure as stated for 'ctl3', except use a 5 g Class S calibration weight. Perform the other control weighings in this way as they occur throughout the sample worksheet. Control weighings must be within ±0.0005 g of the known value. If the control difference limit is exceeded, the previous nine filters and duplicate must be re-weighed.

9.6 Using powder-free antistatic gloves, remove the first filter from its folder and carefully place it onto the filter holder on the balance pan. Make sure the filter number recorded on the Sample Report form agrees with the number on the filter. Close the glass door and wait for the balance to stabilize. The weight should be stabilized for a minimum of five seconds before transferring the weight to LimsLink™ by pressing the 'PRINT' button on the balance.

9.7 Copy the weight displayed in LimsLink™ onto the Sample Report form. Remove the filter from the balance and return it to its folder. Close the glass enclosure and make sure that the balance display reads 0.0000 g.

9.8 Repeat Sections 9.6 and 9.7 for the remaining filters. Duplicates (denoted by Rep # 2 in LimsLink™) are weighed in precisely the same manner; record the weight on the Sample Report form above the first post-weight value. The duplicate difference limit for PM_{10} post-weights is ±0.0050 g. If the duplicate difference limit is exceeded, the previous nine filters and duplicate must be re-weighed.

9.9 When post-weighing is complete, click on the 'Options' menu, 'Report1', then 'Add Duplicates to LIMS'. After a few minutes click on the 'Options' menu, 'LabODB3C', then 'Retrieve Sample Status'. The status of all post-weights in LimsLink™ should now be 'OK to Transfer'. Click on the 'Options' menu, 'Report1', then 'Send Post-Wts to LIMS'. The field to the right of the sample status should now read 'Sent to LIMS'. After a few minutes click on the 'Options' menu, 'LabODB3C', then 'Retrieve Sample Status'. The sample status should now say 'Complete'.

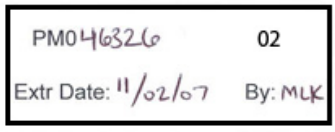
9.10 When the status of all samples is 'Complete', a report is run in order to verify that all QC parameters were met. Double-click on the desktop shortcut 'Reports' and login. Click on 'File', 'Run', and double-click on 'PM10-PostWeight Summary.rep'. Enter the correct date and select the correct balance name from the drop-down menu. Click on the green stoplight icon to run the report. Check the report to verify that duplicates are acceptable (± 0.0050 g), the duplicate

percentage is acceptable (≥10% according to the MLD NLB Laboratory Quality Control Manual (June 2001, rev. 2.4)), and control weighings are acceptable (±0.0005 g of the known value). Although the duplicate percentage must be ≥10%, since we perform a duplicate for every nine or fewer samples the duplicate percentage should always be >11.1%.

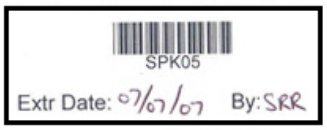
10.0 SAMPLE EXTRACTION PROCEDURE

10.1 Double-click on the desktop shortcut 'Reports' and login. Click on 'File', 'Run', and double-click on the file 'Extraction Worklist.rep'. Select the 'PM10 Extraction' method. Press the green stoplight icon to run the report. Take this extraction worklist into the Extraction Laboratory, along with the folders containing the filters.

10.2 Create a set of extraction labels with the barcodes that correspond to the extraction worklist. The labels should also have the extraction date and the analysts' initials printed on them. For samples that are duplicates, a space followed by '02' is appended to the barcode. See examples below:



10.3 Blanks and spikes equal to the number of duplicate samples on the extraction worklist are extracted along with the samples. Unexposed filter quarters are used as the background media for blanks and spikes. These are located near the cutting board in manila envelopes numbered 1-10 (See Section 3.6). Randomly choose which manila folder(s) to take unexposed filter quarters from, and append these to the worklist. Use labels printed with the corresponding blank or spike identification number (number on the manila folder they are taken from). Write the extraction date in the indicated area and initial the label. See examples below:



10.4 For each sample, blank, and spike listed on the extraction worklist, place an Erlenmeyer flask on a moveable cart. Fold down one corner of each of the prepared labels and affix them firmly to the

Erlenmeyer flasks. (Folding the corner makes the labels easy to remove after shaking.)

10.5 If there is an insufficient amount of water to perform the extractions in the dispensing jug, fill the jug to the fill line (about 15 liters) with nanopure water. Connect the jug to the Wheaton Unispense® II water delivery system and deliver water to waste until all air bubbles have been cleared out of the line. (Tilting the jug will aid in the release of air bubbles trapped near the outlet.)

10.6 Unispense Calibration:

The Wheaton Unispense® II water delivery system must be calibrated every time more nanopure water is added to the dispensing jug. This is done using the Excel spreadsheet named 'Unispense Calibration' that is located on the desktop attached to balance A200SA in the balance room. Five empty numbered sample bottles are located next to the Unispense®. Weigh them when dry, and record the weights in the spreadsheet. Dispense water into the sample bottles using the Unispense® and weigh them again. Record the weights in the spreadsheet. The spreadsheet automatically calculates the mean volume and standard deviation. The acceptable volume range is 99.5 – 100.5 mL with a standard deviation of ± 0.5 g. If the calculated values fall outside of this range the Unispense® must be adjusted accordingly (see the Wheaton Unispense® II operators manual) and recalibrated.

10.7 Using a clean, dry laboratory wipe, thoroughly clean the cutting board blade and scissors. Place clean, dry laboratory wipes around the immediate cutting area to prevent contamination.

10.8 Use the cutting board to cut a 3 1/2" x 4 1/2" section of the exposed area of each filter. Remove a filter from its manila folder using powder-free antistatic gloves and place it lengthwise on the cutting board, exposed-side up, with the factory-stamped number on the right side. Line the left margin of the exposed area up with the 4 1/2" line of the cutting board and cut the filter. (Note: If the exposed area is not centered on the filter this technique will still produce two equal exposed-area halves.) Rotate the left half of the filter 90 degrees counter-clockwise, line the left margin of the exposed area up with the 3 1/2" line of the cutting board and cut the filter. These two cuts will produce a section of filter containing one quarter (3 1/2" x 4 1/2") of the original exposed area. Never remove the section imprinted with the factory-stamped number; this section must be retained for identification purposes. Place the remaining three-quarters of the filter back into the glassine enclosure, making sure that the stamped

filter number is visible through the glassine.

10.9 Cut the 3 1/2" by 4 1/2" section in half and fold it such that the sampled area is contained inside and is never touched with your gloves. Cut in half and fold two more times. Using the long-edge scissors, cut the filter into approximately equal-sized pieces directly into the Erlenmeyer flask labeled with the corresponding barcode. Blank and spike filters are pre-cut in quarters in manila folders next to the cutting board. These filters should also be cut into approximately equal-sized pieces directly into the appropriate Erlenmeyer flask. Dispense 100.0 mL of nanopure water into each Erlenmeyer flask and seal it with a ground glass stopper.

10.10 For spikes, use the micropipettor to remove 1.0 mL of water from the flask and add 1.0 mL of spike solution. See spike solution concentrations below.

ANALYTE	CONCENTRATION
$[Cl]^-$	200 µg/mL
$[NO_3]^-$	1000 µg/mL
$[SO_4]^{2-}$	1000 µg/mL
$[NH_4]^+$	200 µg/mL
$[K]^+$	220 µg/mL

10.11 Repeat Sections 10.7 through 10.10 for the remaining samples on the extraction worklist. For duplicate samples, use the section of filter diagonally opposite the originally removed section.

10.12 Secure the stoppered Erlenmeyer flasks on the shaker table and shake them for 60 minutes at low speed (approximately 120 excursions/minute).

10.13 After the samples, blanks, and spikes have shaken for 60 minutes, the extraction solutions are vacuum filtered in the order shown on the extraction worklist. Gloves should also be worn throughout the vacuum filtration process in order to prevent contamination.

10.14 Thoroughly rinse the magnetic filter funnel with nanopure water. With the vacuum on, insert the bottom piece of the magnetic filter funnel into the filter dome. Then add the filtration membrane and the top piece of the filter funnel. Pour about 75-100 mL of nanopure water into the funnel to wet and rinse the surface of the membrane. Ensure

that all rinse water is removed by breaking the vacuum and re-applying it one or more times as necessary. Discard the rinse water down the drain.

10.15 Immediately prior to filtering, transfer the label from the samples' Erlenmeyer flask directly to the individual sample bottle into which the filtrate will be stored. The label should adhere firmly and completely to the bottle. Place the labeled bottle underneath the filter funnel.

10.16 Swirl the contents of the flask and then pour the solution, along with filter pieces, into the filter funnel. Let the vacuum pull the liquid through the membrane into the sample bottle. Place a screen in the sink to collect filter pieces and prevent them from clogging the drain. Remove any filter pieces remaining in the flask by rinsing the flask with water, and then pouring it into the sink.

10.17 After the liquid has been pulled through, disconnect the apparatus carefully and seal the labeled bottle with a clean lid.

10.18 Discard the used membrane and rinse both parts of the filter funnel thoroughly with nanopure water in order to remove any filter residue or particles. Repeat Sections 10.14 through 10.18 for the remaining samples, blanks, and spikes on the extraction worklist.

10.19 The extraction solutions are now ready to be analyzed by ion chromatography. Place the filled sample bottles in shallow boxes in chronological order. Store the blanks and spikes in a separate box. Store the boxes in a refrigerator set at 40°F to prevent microbial growth.

10.20 Thoroughly rinse the filter funnel with nanopure water and put the vacuum flask, along with the Erlenmeyer flasks and their stoppers, through two steam dishwasher cycles (first with soap added, then without soap).

10.21 Sending Extraction Dates to LIMS:

After the samples have been extracted the extraction dates must be transferred into LIMS. Login to LimsLink™ and click on the running man icon. Select the 'Extraction Date Transfer' method, then click 'Start New' in order to create a new worksheet. A window will pop up with a 'Description' field; enter the name of the new worksheet. The worksheet name should be the date followed by the analyst's login name, e.g., 11/11/07 mmonroe. Click 'OK'. Click on the 'Options' menu, 'LabODB3C', then 'Get PM10 Extractions'. A list of all samples that need to be extracted will be

generated. Enter the extraction date next to the samples that you have extracted. The status of the extracted samples in LimsLink™ should be 'OK to Transfer'. Click on the 'Options' menu, 'Report1', then 'Send EXTR Dates to LIMS'. The field to the right of the sample status should read 'Sent to LIMS'. After a few minutes click on the 'Options' menu, 'LabODB3C', then 'Retrieve Sample Status'. The sample status should be 'Complete'.

10.22 Cleaning Extraction Sample Bottles:

10.22.1 After the samples have been analyzed they can be discarded. Remove the bottle caps, rinse them with tap water, and soak them overnight in a 4-liter beaker filled with tap water and 50 mL of bleach. Empty the contents of the sample bottles down the sink and rinse them out with tap water. The affixed labels are removed and discarded as well. Place the sample bottles upright in the sink (make sure the drain stopper is securely seated). Cover the bottles with metal racks and place an additional layer of bottles on top of the metal racks. Cover the second layer with metal racks and use the 4-liter beaker filled with sample bottle caps as a weight to prevent the bottles from floating. Fill the sink with tap water and 300 mL of bleach and soak overnight.

10.22.2 After soaking overnight, rinse both the bottle caps and bottles thoroughly with tap water and place them in the dishwasher. Wash them on a setting that is suitable for plastic (without steam) using non-foaming detergent, then wash them again on the same setting, but with no detergent. Rinse them thoroughly with nanopure water and air-dry. Store them in a dust and contaminant-free environment until they are reused.

11.0 ARCHIVING OF PM_{10} SAMPLES

After PM_{10} samples undergo gravimetric analysis they are organized by barcode and placed in archive boxes with lids. Archive boxes containing samples from the previous three to four months are stored in the room in which extractions are performed. Older samples are stored elsewhere (currently rooms 101 and 205). Samples are retained until five years from the sampling date, at which time they are disposed of. See MLD NLB QC Manual Revision 2.4 for more information.

12.0 REFERENCES

12.1 U.S. Environmental Protection Agency. 1997. Code of Federal Regulations, Title 40, Part 50, Appendix B. Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method).

12.2 U.S. Environmental Protection Agency. 1997. Code of Federal Regulations, Title 40, Part 50, Appendix M. Reference Method for the Determination of Particulate Matter as PM_{10} in the Atmosphere.

12.3 U.S. Environmental Protection Agency. 1997. Quality Assurance Guidance Document 2.11, Monitoring PM_{10} in Ambient Air Using a High-Volume sampler Method.

Appendix A: INSPECTION OF QUARTZ FILTERS FOR PM_{10} SAMPLING

1.0 SCOPE

After receipt from U.S. EPA, all filters are inspected for physical defects before they are sent to sampling sites. This document presents the criteria for the acceptance or rejection of the filters, as adapted from guidelines received from the U.S. EPA, Atmospheric Research and Exposure Assessment Lab, QA Support Branch, October 23, 1991.

2.0 PRECAUTIONS

Quartz filters have low tensile strength and are somewhat brittle. They should be handled carefully during inspection to prevent tearing, breaking, or loss of fibers. To prevent contamination of the quartz filters, powder-free antistatic gloves must be worn when filters are handled. Filters should be protected from dust and other contaminants.

3.0 INSPECTION METHOD

All filters are inspected using a light screen or table, with critical inspection of both the front (the side with no factory stamped number) and the back (the side with the factory stamped number) of the filter. Filters should also be inspected without the aid of a light table, as some defects (such as indentations) are only visible under ambient lighting. Appendix A, Sections 4 and 5 describe the visual defects used to determine the acceptance/rejection of each filter. The same criteria are also used for the inspection of glass filters used for TSP sampling.

4.0 REJECTION CRITERIA:

a) Hole - a hole that goes completely through the filter. A filter containing a hole of any size is rejected.

b) Dense Spot - viewed from the filter front, this appears as a dark area (approximately 1/8"-1/4" in diameter) without sharply defined edges. Viewed from the back, an accumulation of filter fibers can be seen. A filter with more than one dense spot is rejected.

c) Dark Spot - a defect similar to a dense spot, but smaller in diameter. A filter with more than two dark spots is rejected.

d) Loose Fiber- this appears as if a rough object has moved across the filter and loosened the filter base. If the fibers are large and/or too numerous to remove without damaging the filter then the filter is rejected.

e) Detached Fibers - when viewed from the front this defect resembles a thin spot. The shape can be circular or oval; no evidence of this defect can be seen from the back. Gently rub the filter to remove the detached fibers. If this creates a hole, the filter is rejected.

f) Coloration - yellow, red, black, or other colored spots may appear. A filter with such coloration is rejected.

g) Other - filters with any obvious structural imperfection not described above such as frayed edges, torn corners, indentations, pronounced creases or other results of other poor workmanship are rejected.

5.0 ACCEPTABLE IMPERFECTIONS

a) Line - occasionally a fine line created by the manufacturing screen appears across the filter. A filter with such a line is acceptable.

b) Thin Spot - a small area (slightly larger than a pinhole) viewed from the filter front that appears to be weak. More light can be seen through this area than through the surrounding area. Viewed from the back there is no evidence of this problem. Acceptance testing performed by the U.S. EPA has shown that filters with thin spots are acceptable for use.

Appendix B: QUALITY CONTROL CRITERIA FOR PM_{10} SAMPLES

1.0 SCOPE

This appendix lists the quality control invalidation criteria for PM_{10} quartz filter samples collected on SSI samplers. All samples collected in the field are to be checked using these criteria. Samples not meeting these criteria are invalid. The criteria listed supersede and replace any inspection criteria published prior to November 1996. The same criteria listed here for PM_{10} filters are also used for TSP glass filters.

2.0 PM_{10} SAMPLE INVALIDATION CRITERIA

a) Filter Contamination

Filters that are dropped or become contaminated by any foreign matter, e.g., dirt, fingerprints, ink, liquids, etc., are invalid.

If insects are embedded in the sample deposit, remove them using Teflon®-tipped forceps. Disturb the sample deposit as little as possible during this process. Samples with embedded insects will be considered for validation on a case-by-case basis. In instances where there is little or no apparent loss of deposited mass due to the removal of the insects the sample will be made valid. If a significant loss of deposited mass is apparent then the sample will be invalidated.

b) Damaged or Torn Filters

Filters with tears or pinholes that occurred before or during sampling are invalid. Filters missing any part of the exposed area are invalid.

Quartz filters missing unexposed pieces of corners or edges are invalid. If unexposed pieces of corners or edges are torn off, but are included in the returned sample package, the sample is valid. Glass filters missing unexposed pieces of corners or edges are valid.

c) Filter Leakage

If the filter shows signs of air leakage due to a worn or improperly seated gasket, the sample is invalid. Gasket leakage is discernible as a dark streak along the edge of the filter.

d) Dickson Chart

A complete Dickson chart, documenting the flow rate through the sampler for 24 hours, must be submitted to the laboratory with each filter sample. Filter samples without complete Dickson recorder chart records are invalid, with the following exceptions:

Volumetric Flow Controlled Samplers (VFC)

In cases of inking problems where the trace is not complete for 24 hours, the sample will be considered valid if the previous sample and subsequent sample are valid with complete chart traces. In instances when either the previous or subsequent sample is invalid, the operator must provide substantiating information for validating the sample. These samples will be considered for validation on a case-by-case basis.

Mass Flow Controlled Samplers (MFC)

The flow rates of MFC samplers are generally not as stable as VFC samplers. Due to this, a complete Dickson chart trace is of greater importance for MFC samples. In cases of inking problems where the trace is not complete, the sample will be considered valid if: 1) start and stop marks are evident to verify start and stop times; 2) no more than three consecutive hours of trace are missing and the trace appears to be at the same value at either end of the skip; and 3) the operator validates that the sampler operated properly. Samples not meeting these three criteria will be considered for validation on a case-by-case basis.

e) Start/Stop Times

The sampler start and stop time must be 0000 (midnight) $\pm$ 30 minutes. If the Dickson chart and/or the time recorded on the Sample Report form indicates that the sampler began before 2330 hours or after 0030 hours, the sample is invalid unless the operator can determine that the error in start/stop time was the result of an error in the recorder pen alignment. In such cases the operator should verify the correct start/stop time in the Comments section of the Sample Report form.

f) Sample Run Duration

Samples must be collected for 1380 – 1500 minutes. Samples collected for less than 1380 minutes or more than 1500 minutes, as documented by the Dickson chart and/or the elapsed time meter, are invalid.

g) Power Failure

If a power failure during a sample run causes the start/stop time or sample run duration requirements to be violated, the sample is invalid. Short-term power outages, however, do not make a sample invalid unless the sum of these outages exceeds one hour.

h) Sample Flow Rate

If the flow rate through the sampler is outside the accepted range for the site for more than one hour during the sampling period, the sample is invalid. This includes irregular flow rate excursions and the sampler warm-up stabilization period. The acceptable flow rate range for PM_{10} samples is 36 - 44 Cubic Feet per Minute (CFM) and Standard Cubic Feet per Minute (SCFM), and the acceptable flow rate range for TSP samples is 39 - 60 CFM and SCFM. Please note that the CFM and SCFM must both be within the acceptable range or the sample is invalidated. The acceptable flow rate range is adjusted for altitude if the sampling site is more than 1000 feet above sea-level.

i) Report Form

The filter is considered invalid if a Sample Report form is not included with the sample. If the Sample Report form is incomplete then the site operator should be contacted in order to obtain the missing information. If the information is not available the sample is invalidated.

j) Date Sample Received in Lab

PM_{10} samples are invalid if they are received more than 30 days from the sampling date.

k) Wrong Filter or Media Used in Sampling

Any sample received with the filter number on the sample report form not matching the filter number stamped on the enclosed filter is invalid. A PM_{10} sample is invalid if a glass filter is used. Conversely, A TSP sample is invalid if a quartz filter is used.